

Final Technical Report

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Fundamental Investigations of the Tribological Properties of Biological Interfaces

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2. Objectives: (As stated in original proposal)

The **objective** of the proposed program is to understand the fundamental nature of forces existing at solvated polymer-polymer and protein-terminated polymer-polymer interfaces under shearing conditions, thereby allowing the future design of biological/bioinspired tribological systems lubricated by aqueous solutions. The proposed experimental program will be aimed at measuring interfacial forces over a range of length scales, for sets of systematically prepared and well-characterized polymer and biopolymer interfaces. This program will also explore the influence of solvent conditions on the measured interfacial interactions. The proposed program will explore the role of polymer architecture (composition and structure) in determining the adsorption, load-bearing, and frictional properties of self-assembling waterborne organic coatings. It will also examine the lubricious properties of a number of different adsorbed proteins, suspected to be tribologically active in biological systems. The fundamental **goal** of the program is to elucidate the modes of interaction between polymer surfaces (penetration, repulsion, compression) and the role of solvent (related to polymer swelling and conformational changes) in modifying interactions between the polymer surfaces. The applied aim of the program is to provide design criteria and performance limitations of low-friction biological and/or bioinspired interfaces.

3. Nature of Effort:

During the course of this project, we have focused on developing a molecular level understanding of the tribological properties of polymer brush systems and the relationship between these properties and issue of surface chemistry and solvation. Studies have been conducted on both the microscopic and macroscopic length scales. Success has been realized through the control of polymer architecture via synthetic routes and has provided the means for systematic and fundamental studies of polymer properties in aqueous media. Work has incorporated a broad range of experimental tools, providing a detailed picture of these interfaces and the basis for molecular level interpretations. The specific results of these studies and their potential impact are described in the following sections of this report.

4. Accomplishments

4.1 Polymer synthesis

A number of PLL-g-PEG copolymers have been synthesized to provide architecture variations and allow investigating the relation of solvation and friction of the absorbed polymer layer in HEPES buffer solution and in organic solvents. The newly synthesized polymers include PLL(20)-g[2.9]-PEG(2), PLL(20)-g[3.4]-PEG(2), PLL(20)-g[3.4]-PEG(5), PLL(20)-g[5.7]-PEG(2), and PLL(350)-g[3.4]-PEG(5), PLL(20)-g[5.8]-PEG(10), PLL(20)-g[7.6]-PEG(10), PLL(20)-g[15.7]-PEG(10), PLL(5.2)-g[5.2]-PEG(5), PLL(20)-g[8.0]-PEG(5), PLL(20)-g[11.8]-PEG(5), PLL(20)-g[3.3]-PEG(2) and PLL(20)-g[8.0]-PEG(2). A brief description of the synthesis process is as follows: poly(L-lysine) hydrobromide (84 mg, mol. wt. 20 kDa, Sigma, USA) was dissolved in 1.05 ml of 50 mM sodium borate buffer solution and the solution was filter sterilized (0.22 μ m pore-size filter). For the grafting of PEG onto PLL, the N-hydroxysuccinimidyl ester of methoxypoly(ethylene glycol) propionic acid (216 mg, mol.wt. 2

kDa, SPAPEG, Shearwater Polymer, Inc., USA) was added to dissolved PLL. The reaction was allowed to proceed for 6 hr at room temperature, after which the reaction mixture was dialyzed (Spectra-Por, mol. wt. cutoff size 6-8 kDa, Spectrum, Houston, TX, USA) for 24 hr, first against phosphate-buffered saline (PBS, pH 7.4) and subsequently against deionized water. The product was freeze-dried and stored at -20°C .

4.2 Macrotribology

4.2.1 Lubrication of oxide surfaces

The formation of a lubricating boundary layer of PLL-g-PEG and the corresponding frictional properties at oxide interfaces were investigated by ultra-thin film interferometry and mini-traction machine (MTM) under a high-pressure contact. Both approaches provide a rolling contact (sliding component lower than 2.5% in 100% scale) between a loaded stainless-steel ball (radius $R = 9.5$ mm, AISI 440, $R_a = 11$ nm) and a flat surface of a silicate glass disk ($R_a = 2$ nm). Figure 1 compares the coefficient of friction (COF) and the boundary layer film thickness of polymer-free HEPES buffer solution, PLL(20)-, and PLL(20)-g[3.4]-PEG(2)-containing HEPES buffer solution at a steel/glass tribo-pair.

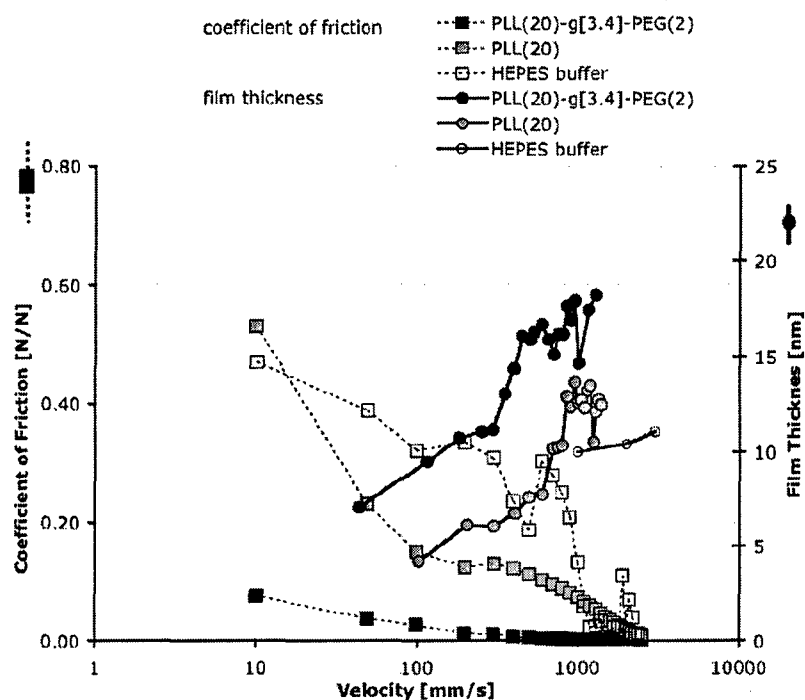


Fig.1: A direct comparison of the coefficient of friction (y-axis on the left side) and the lubricant film thickness (y-axis on the right side) of an FeOx/SiOx tribo-pair when lubricated by HEPES buffer solution and PLL-g-PEG-containing aqueous solution (PLL-g-PEG 0.25mg/ml).

The film thickness of pure HEPES buffer solution could not be reliably measured below 1 m/s due to significant wear and resulting damage to the glass disc. However, upon addition of PLL(20)-g[3.4]-PEG(2) to the pure HEPES buffer solution, no such damage occurred and the film thickness was found to increase from 7 to 18 nm as the velocity was increased from 0.01 to 1 m/s. The coefficient of friction vs. velocity plot obtained for pure HEPES buffer solution shows a constant COF of ~ 0.5 at velocities below 1 m/s. However, at higher velocities, the COF became unstable and oscillated with a high irregular amplitude between 0.1 and 0.01. On the other hand, PLL(20)-g[3.4]-PEG(2) solution displayed a quite uniform decrease of the COF over the whole velocity range, to reach values at least an order of magnitude lower than those obtained from pure HEPES buffer solution. Film thickness and friction results clearly indicate the ability of PLL-g-PEG to form a stable boundary lubrication film leading to a significant reduction of the coefficient of friction compared to pure HEPES buffer solution.

The influence of the architectural parameters of the PLL-g-PEG polymers on film formation and friction was investigated by varying the side-chain (PEG) length, the Lys/PEG grafting ratio, and the backbone (PLL) length. As shown in Fig. 2, both increasing the molecular weight of the PEG side chains and reducing the grafting ratio were found to result in a significant improvement in the lubricating properties of aqueous PLL-g-PEG solutions. Increasing the molecular weight of the PLL backbone resulted in an increase of the coefficient of friction at intermediate-to-high velocities, but had little effect on film thickness (data not shown).

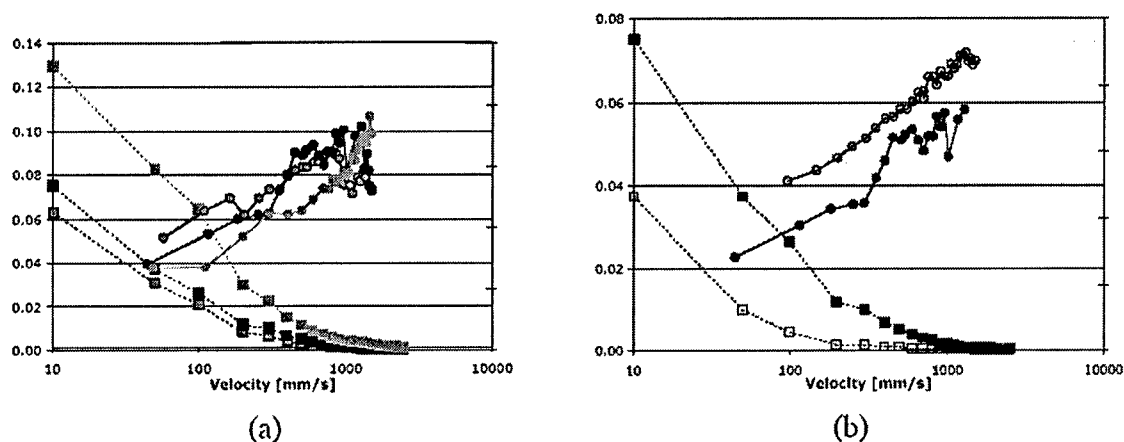


Fig.2 The influence of the PLL-g-PEG architecture on the tribological properties of FeOx/SiOx interface; (a) molecular weight of the PEG chains (2 kDa., and 5 kDa.) and (b) Lys/PEG grafting ratio (2.2, 3.4, and 5).

4.2.2 Biotribology

Following the studies on the conformation change in bulk solution and the aqueous-lubrication properties for PDMS/PDMS sliding as reported in the previous report, the adsorption behavior of porcine gastric mucin (PGM) have been investigated as a function of pH and ionic strength. For the correlation with the lubricating properties of PGM for the self-mated PDMS interface, the *in-situ* adsorption behavior of PGM onto a PDMS surface in aqueous environment was investigated by means of optical waveguide lightmode spectroscopy (OWLS). In this approach, the mass of adsorbed molecules on top of a waveguiding layer is estimated by

monitoring the refractive index change upon injection of polymer solution into the cell where polymer-free buffer solution is in optical equilibrium. The waveguiding layer, which is comprised of $\text{SiO}_{0.75}\text{TiO}_{0.25}$ on a glass substrate, was further coated with ultra-thin layer of PDMS film (ca. 30nm) by spin coating. The results for the adsorption properties of PGM at PDMS surface are presented in Figure 3.

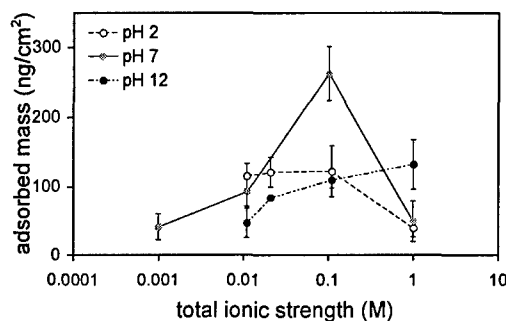


Figure 3. The adsorption properties of PGM onto PDMS surface in aqueous environment as a function of pH and ionic strength as characterized by OWLS. The concentration of PGM was 1mg/ml.

For both pH 7 and 12, where PGM is negatively charged in aqueous environment, an increase of adsorbed mass with increasing ionic strength (up to 0.1M) was observed. In contrast, for pH 2, where PGM is nearly neutralized, the adsorbed mass was virtually not influenced by the change of ionic strength (also up to 0.1M). This behavior is rationalized by the screening effect of salts on the adsorption of polyelectrolyte on a neutral surface; with increasing salt concentration, the accumulated negative charges of the pre-adsorbed PGM can be more effectively shielded, and thus a higher amount can be adsorbed. A rapid drop of adsorbed mass at even higher ionic strength (1.0M) for pH 2 and 7 needs to be further understood, however.

At an ionic strength of 0.1M, pH 7 showed a higher amount than pH 2 and 12. However, the lubricating properties exhibited an opposite trend as shown in Figure 4.

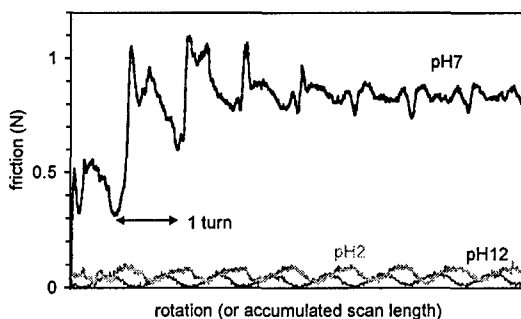


Figure 4. The friction force vs. number of rotation plots for the PGM-solution-lubricated sliding of PDMS/PDMS as a function of pH by means of pin-on-disk tribometry (applied load was 1N and salt concentration was 0.1M).

While the PGM-solution-lubricated sliding of PDMS/PDMS at pH 2 and 12 revealed very low friction forces from the very initial contact, the corresponding sliding at pH 7 showed a stepwise increase of friction forces in a first few rotations, followed by steady and higher friction forces. This observation suggests that some weakly bound adsorbate layer might be removed or stressed in the “running-in” period for pH 7, and does not effectively contribute to lubrication. In other words, it is not simply the amount of adsorption that determines the lubricating properties of PGM solution for this tribosystem, but many other factors may play a significant role as well. To propose a model to account for the contradiction, at pH 2, circular dichroism (CD) studies implied an aggregation of PGM in bulk solution, and thus a flat conformation is expected due to multiple binding of the aggregated PGM onto surface. This would reduce the adsorption amount, yet provides a higher stability of PGM at surface. Meanwhile, at pH 7, no such aggregation is detected by CD, and thus a relatively higher amount of PGM, yet reduced stability is expected at surface. At pH 12, the conformation of PGM at surface may be closer to that at pH 7. However, the repulsion between two surfaces carrying the same strong charge may also contribute to lubrication. A further understanding of the detailed lubrication mechanism is needed in the future.

4.2.3 Aqueous lubrication of elastomers: influence of surface modification

For lubrication involving water as a lubricant, where an increase of viscosity of the lubricant under pressure is nearly unexpected, employment of elastomers as tribopair can be an approach to enable effective lubrication, i.e. activation of isoviscous-elastic lubrication (or soft-EHL). In fact, the remarkable lubricating performance of natural articular joint has also been ascribed, in large part, to the compliance of cartilage rather than just to the composition of synovial fluid itself. The soft-EHL, however, is often hindered by the surface roughness or other surface properties such as adhesion, especially at low speeds. For this reason, extensive efforts have been taken to modify the surface properties of a model elastomer, PDMS, in various ways.

Oxygen-plasma-treatment. Figure 5 shows an effect of oxygen-plasma-treatment of PDMS surface on the aqueous lubrication properties.

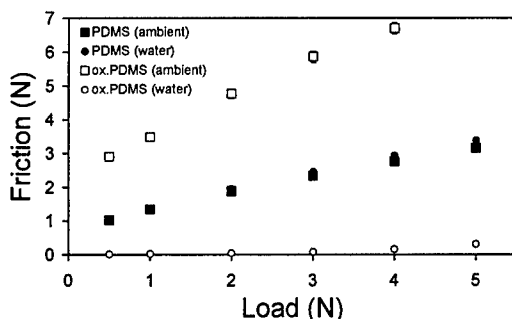


Figure 5. Friction vs. load plots for the self-mated sliding of PDMS in distilled water. The radius of sphere was 3mm, the sliding speed was 0.005m/sec, and the sample was exposed to oxygen plasma for 1 minute.

For untreated PDMS, the interfacial friction for self-mated sliding was extremely high in ambient and was not reduced even upon immersion in water. For the oxygen-plasma-treated PDMS (*ox*-PDMS), however, an enormous reduction of the interfacial friction was observed in water, while an opposite trend was observed in ambient. Oxygen-plasma treatment is known to

cause a hydrophilization of the PDMS surface by introducing hydroxyl groups onto the surface, yet no significant change in bulk mechanical properties. The dramatic influence of oxygen-plasma treatment upon aqueous lubrication of PDMS is thus attributed to the removal of strong hydrophobic interaction between two PDMS surfaces, and facilitates a formation of an aqueous lubricating film. The increased friction forces of *ox*-PDMS in ambient can be also understood in terms of a strong hydrophilic interactions in hydrophobic media.

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide): PEO-PPO-PEO.

Given the effect of oxygen-plasma treatment on the aqueous lubrication of PDMS, amphiphilic copolymers such as PEO-PPO-PEO or PLL-g-PEG can be employed as an alternative to the hydrophilization of the PDMS surface. While the adsorption of PLL-g-PEG is known to be most effective at negatively charged surfaces in aqueous environment, PEO-PPO-PEO has been well characterized to adsorb onto hydrophobic surfaces, and thus is suitable to modify PDMS surface without other treatment. In spite of a wide range of applications of this commercially available copolymer (BASF Co.) for other fields outside tribology, the information on the lubricating properties, especially for aqueous lubrication, is extremely rare. For this reason, we performed comparative adsorption and lubrication studies employing a series of copolymers possessing a systematically varying PPO molecular weight and PEO/PPO ratio. The relationship for the adsorption and lubrication properties is shown in Figure 6.

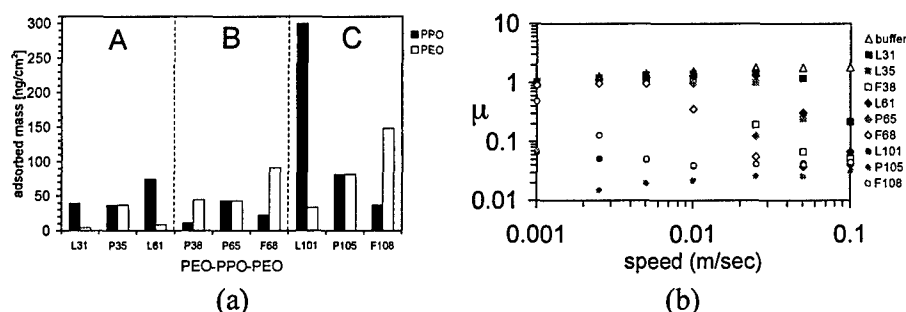


Figure 6. (a) The adsorption properties (OWLS) and (b) the lubricating properties (pin-on-disk tribometry) of PEO-PPO-PEO copolymers for PDMS surface. The applied load for the pin-on-disk measurements was 1N.

In Figure 6, the nomenclature for the copolymer stands for the physical state (L for liquid, P for past, F for flake), the molecular weight of PPO block (first or (first two) number(s) times 300 leads to approximate m.w. of PPO block), and the PEO molecular weight ratio (the last number times 10 leads to % ratio of PEO). In Figure 4(a), the adsorbed mass for each PEO-PPO-PEO copolymer was decomposed into that of PEO (white bar) and PPO (black bar) block. In addition, the copolymers exhibiting similar lubricating properties are grouped together along the x-axis (see Figure 4(b) for more details); the group A, exhibiting a negligible reduction effect over 0.001 to 0.1m/sec range, the group B, exhibiting a reduction in μ only from high speed (> 0.05 m/sec), and the group C, exhibiting an effective reduction in μ from the lowest speed (> 0.001 m/sec). A careful comparison of adsorption properties of PEO and PPO block and the lubricating properties showed that it is the formula weight or adsorbed mass of PPO block that primarily determines the lubricating properties, yet an additional role of PEO is also observed. This is because a stable anchoring of the copolymer onto surface must be guaranteed first, i.e. the

significance of m.w. of PPO block, to allow a hydrophilic PEO block to favorably interact with water for lubrication.

PLL-g-PEG. Previously, the application of PLL-g-PEG as an aqueous lubricant has been mostly for oxide tribosystems. The model elastomeric tribosystem, PDMS, has also been found to be capable of being effectively coated with PLL-g-PEG, and thus the desired aqueous lubricating effect can be achieved. As mentioned in the previous report, amino groups in PLL backbones possess not only positive charges ($-\text{NH}_3^+$), but also reasonably long hydrophobic groups ($-(\text{CH}_2)_4-$). Therefore, two approaches to immobilizing PLL-g-PEG copolymer onto PDMS surface have been employed, firstly via electrostatic and secondly via hydrophobic interaction.

Firstly, oxygen-plasma treatment of PDMS surface produces hydroxyl groups on the PDMS surface, negative charges are therefore generated in an aqueous environment, and thus PLL-g-PEG is adsorbed onto *ox*-PDMS surface in a similar way with onto other oxide surfaces. When the friction measurements were performed immediately after the surface modification, a further modification of *ox*-PDMS surface with PLL-g-PEG (PLL(20)-g[3.4]-PEG(5)) exhibited an excellent, yet indistinguishable aqueous lubricating effect compared with bare *ox*-PDMS (see Figure 5 below). However, a distinctive difference was observed when the friction measurements were performed after both surfaces have been exposed to ambient environment for one week as shown in Figure 7.

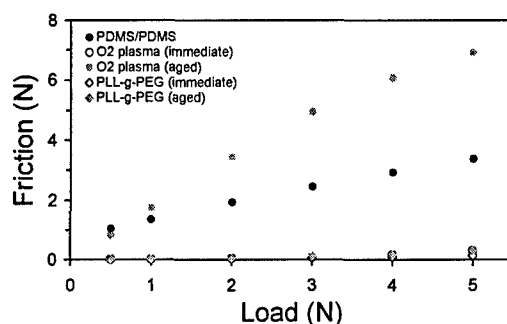


Figure 7. The friction vs. load plots for the self-mated sliding of PLL-g-PEG-coated and bare *ox*-PDMS surfaces in distilled water. A distinctive contrast of the aging effect in ambient (one week) is presented.

While PLL-g-PEG-coated *ox*-PDMS preserved excellent aqueous lubricating properties even after aging in ambient for one week, bare *ox*-PDMS showed a clear degradation in aqueous lubricating properties. This is attributed to the hydrophobic recovery of *ox*-PDMS in ambient. It is well known that the hydrophobic recovery of an *ox*-PDMS surface induces a restructuring of hydrophilic (OH-) and hydrophobic (CH₃- or CH₂-) moieties at PDMS surface, and often accompanies a fracture of glass-like structures of the surface. In contrast, the coating of *ox*-PDMS surface with PLL-g-PEG appears to prevent this process effectively. Thus, the primary benefit of further modification of *ox*-PDMS with PLL-g-PEG is the preservation of surface hydrophilicity (water contact angle $\sim 30^\circ$).

Secondly, the PLL-g-PEG can be adsorbed onto untreated PDMS surface through hydrophobic interaction. However, extensive control experiments revealed that a relatively long

PLL backbone structure, such as PLL(350)-g[3.4]-PEG(5), is required to ensure an effective adsorption and an effective aqueous lubricating effect. Other standard architectures, such as PLL(20)-g[3.4]-PEG(2) or PLL(20)-g[3.4]-PEG(5) did not show an effective lubrication. This observation supports that the main driving force for the adsorption of PLL-g-PEG onto untreated PDMS is hydrophobic interaction, i.e. the adsorption scales with the number of anchoring groups $-(\text{CH}_2)_4-$. The results for the adsorption and lubrication properties of PLL(350)-g[3.4]-PEG(5) as a function of pH and ionic strength are presented in Figure 8.

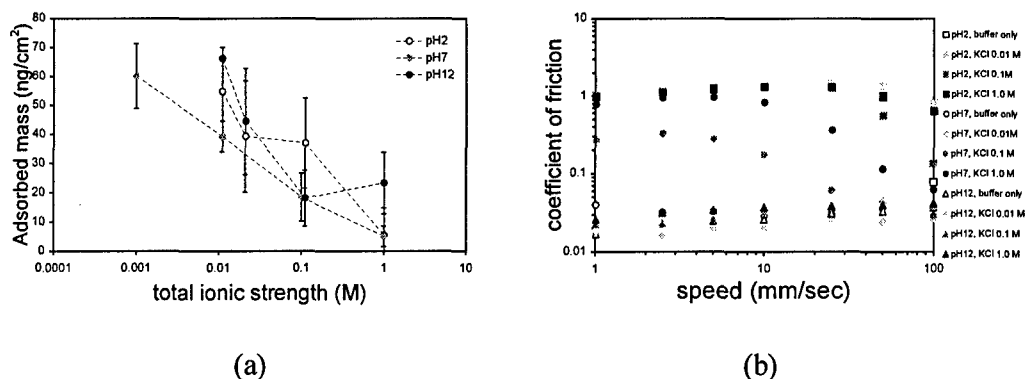


Figure 8. (a) The adsorption and (b) the aqueous-lubricating properties of PLL(350)-g[3.4]-PEG(5) as a function of pH and ionic strength investigated by OWLS and pin-on-disk tribometry, respectively.

While the aqueous lubricating properties showed an interesting dependence on both pH and ionic strength (for instance, excellent lubricating effect at pH 12 regardless of ionic strength, and negligible lubricating effect at pH 2 regardless of ionic strength, yet at pH 7, systematic dependence upon ionic strength), the adsorption properties showed an exclusive dependence on ionic strength only; decreasing adsorption with increasing salt concentration. An understanding of the correlation between adsorption and lubricating properties is poor at this stage and will be further investigated in the future.

4.2.4 Boundary lubrication of oxides

Conventional boundary lubrication of oxide surfaces has been extended by a new approach. The details involve a comparative tribological study of Si-PEG and PLL-g-PEG and the application of PLL-g-PEG-based aqueous lubrication for alumina.

Si-PEG has found a variety of applications, especially in the biological field, due mainly to the protein resistance of PEG brushes. In contrast to PLL-g-PEG, where electrostatic attraction is a driving force to immobilize the copolymer onto oxide surface, Si-PEG is driven to adsorb onto oxide surfaces through covalent bonding of silanes. While a similar performance in protein resistance was observed from both polymers, a noticeable difference was observed in their tribological properties. Figure 9 shows the coefficient of friction (load = 2N) as a function of number of rotations for the polymer-modified steel/glass tribopairs in HEPES buffer solution polymers.

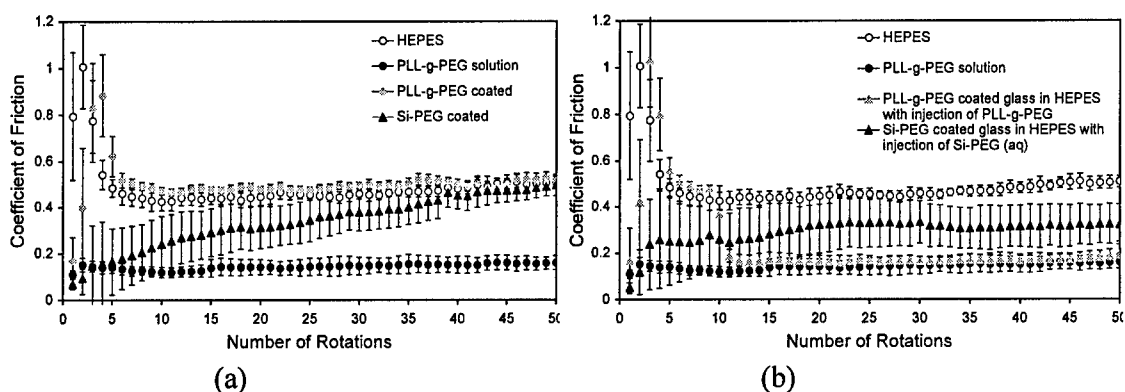


Figure 9. The coefficient of friction vs. the number of rotation for PLL-g-PEG or Si-PEG coated steel/glass tribopair. The load was 2N and the sliding speed was 0.005m/sec.

Figure 9(a) shows the comparison between PLL-g-PEG vs. Si-PEG as well as the presence vs. absence of PLL-g-PEG in bulk solution. While PLL-g-PEG solution (●) exhibited a steadily low coefficient of friction up to 50 rotations, the Si-PEG-coating (▲) showed a gradual increase in the coefficient of friction until it reached a value comparable to that of bare steel/glass pair (○) in HEPES. Excellent boundary lubrication properties of PLL-g-PEG, however, appear to necessitate the presence of the copolymer in buffer solution, since pre-coated PLL-g-PEG without the copolymer in bulk solution (●) exhibited an enormous increase in coefficient of friction after only a couple of rotations. A remarkable difference in tribological properties between with and without PLL-g-PEG in bulk solution is attributed to the fast (re)adsorption, i.e. self-healing, of the copolymer onto the tribologically-stressed track. Figure 9(b) confirms the fast adsorption of PLL-g-PEG in that a high coefficient of friction for the PLL-g-PEG-precoated tribopair (●) rapidly drops upon injection of PLL-g-PEG solution (from ~10th rotation). This effect was not observed from the Si-PEG (▲) as shown in Figure 9(b).

Based upon the successful application of PLL-g-PEG as an aqueous lubricant on silica-based tribosystems, other oxides can also be considered for the PLL-g-PEG-based aqueous lubrication. Alumina is, for instance, widely used for the artificial hip joints as a tribopair, either self-mated or against UHMPE, and the lubrication property is one of the critical parameters to ensure a stable and efficient performance. Some preliminary results for the adsorption and lubricating properties of PLL(20)-g[3.4]-PEG(5) are presented in Figure 10. To characterize the adsorption behavior, alumina was sputter-coated onto waveguiding layer.

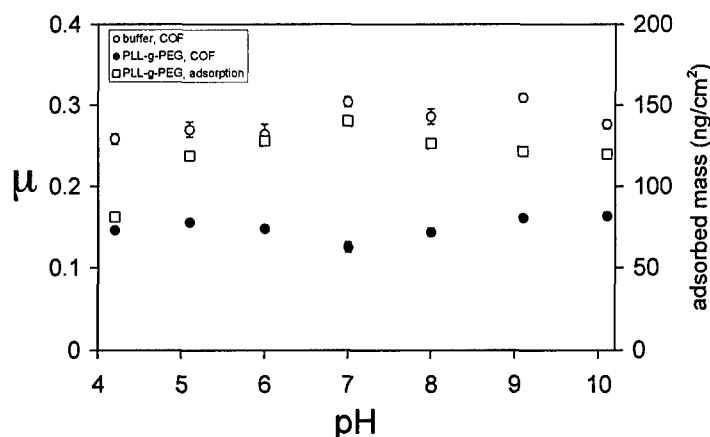


Figure 10. The adsorbed mass and the aqueous lubricating properties of PLL(20)-g[3.4]-PEG(5) for alumina surface as characterized by OWLS and pin-on-disk tribometry, respectively. The load was 5N and the sliding speed was 0.005m/sec. The ionic strength was fixed at 10mM.

For a wide pH range, the adsorbed mass of PLL(20)-g[3.4]-PEG(5) onto alumina surface was observed to be comparable to that onto silica surface. This is abnormal at a first glance since the IEP of alumina lies between pH 8 to 9. Although a further confirmation is needed in near future, however, an accompanying change in lubricating properties supports the validity of adsorption behavior. At present, we do not have a clear explanation on this favorable, yet puzzling adsorption behavior of PLL-g-PEG onto positively charged surface. While the repulsion between positive charges of amino groups and the surface act as a barrier, other driving forces, such as electrostatic attraction between amino groups and coexisting hydroxyl groups together with positive charges on the surface below IEP, may be strong enough to overcome the barrier.

4.2.5 Lubrication of engineering surfaces

As documented in the previous report, the adsorption of PLL-g-PEG polymers onto oxide surfaces is mainly ascribed to the electrostatic attraction between positively charged PLL backbone (amino groups) and negatively charged oxide surfaces in aqueous environment. However, considering the reasonably long alkyl group $-(CH_2)_4-$ in lysine monomer units, one can expect that PLL-g-PEG may adsorb onto hydrophobic surfaces as well, and thus can extend the application of PLL-g-PEG as an aqueous lubricant additive from oxides to hydrophobic surfaces.

The possibility of applying PLL-g-PEG as an aqueous lubricant additive has been tested at various polymer/polymer, polymer/ceramic and polymer/metal interfaces, which are of great significance in modern engineering systems. Polyethylene (PE), polypropylene (PP), polyamide 6,6 (PA-6,6) have been selected to represent the hydrophobic polymer surfaces, and zirconia (ZrO_2) and alumina (Al_2O_3) have been selected for ceramic materials, and finally AISI 440 steel has been selected as a metal surface. The results obtained from pin-on-disk tribometry are summarized in Table 1. For all cases, the COF values reduced upon addition of PLL-g-PEG into aqueous buffer solution (by a minimum of 22.0% for PP/ Al_2O_3 to a maximum of 88.2% for steel/PA-6,6). The reason for the different magnitude of reduction of COF for different tribo-pairs is currently under investigation.

Group	Tribo-pair (pin/disk)	COF buffer only	COF PLL-g-PEG in buffer	Reduction of COF (%)
self-mated polymers	PE/PE	0.43±0.012	0.16±0.004	62.8
	PP/PP	0.49±0.021	0.10±0.009	79.6
	PA-6,6/PA-6,6	0.22±0.003	0.10±0.005	54.5
polymer pins on ceramic or steel disk	PE/Al ₂ O ₃	0.036±0.0036	0.024±0.0024	33.3
	PP/Al ₂ O ₃	0.041±0.0031	0.032±0.0032	22.0
	PA-6,6/Al ₂ O ₃	0.167±0.0030	0.028±0.0010	83.2
	PE/ZrO ₂	0.040±0.0040	0.029±0.0029	27.5
	PP/ZrO ₂	0.065±0.0053	0.036±0.0032	44.6
	PA-6,6/ZrO ₂	0.120±0.0036	0.029±0.0020	75.8
	PE/steel	0.042±0.0039	0.021±0.0027	50.0
	PP/steel	0.077±0.0045	0.030±0.0025	61.0
	PA-6,6/steel	0.113±0.0048	0.018±0.0016	84.1
ceramic or steel pins On polymer disk	ZrO ₂ /PE	0.069±0.0016	0.026±0.0014	62.3
	ZrO ₂ /PP	0.177±0.0087	0.052±0.0015	70.6
	ZrO ₂ /PA-6,6	0.190±0.0070	0.036±0.0013	81.1
	steel/PE	0.056±0.0018	0.025±0.0017	55.4
	steel/PP	0.129±0.0087	0.090±0.0033	30.2
	steel/PA-6,6	0.254±0.0057	0.030±0.0014	88.2

Table 1. Lubrication effects of PLL-g-PEG (0.25 mg/ml in KH₂PO₄ buffer at pH 7) at various polymer/polymer, polymer/ceramic, and polymer/metal interfaces obtained by pin-on-disk tribometry. The load and velocity were fixed at 10N and 5mm/sec respectively. The COFs and standard deviations were obtained by averaging over 1,000 rotations at a given load and velocity.

4.2.6 Lubrication properties of porcine gastric mucin (PGM)

Mucins are the primary macromolecules comprising mucus secretion in various internal organs. Due to their aggregation, often involving gel formation, mucins are known to form a protective layer between the lumen and the cell surface. A schematic of mucin is presented in Figure 11. We pay particular attention to mucin's unique structure, i.e. the combination of very hydrophilic and hydrophobic domains with high molecular weight, in view of their role for lubrication. The hydrophilic domains account for the mucins' water-soluble and water-holding properties, while the hydrophobic domains enable adsorption on hydrophobic surfaces, together suggesting excellent boundary lubrication in aqueous tribosystems.

In the initial stage of the project, we have selected porcine gastric mucin (PGM) in view of its availability (Sigma, St. Louis, MO, USA). The main focus was placed on how the conformation of PGM changes as a function of pH and ionic strength and how these changes are associated with the lubrication properties in corresponding conditions. To understand the conformational change of PGM and its lubrication effect in parallel, circular dichroism (CD) and pin-on-disk tribometry have been employed. Self-mated PDMS has been employed as a model tribo-pair to represent an elastic, hydrophobic interface.

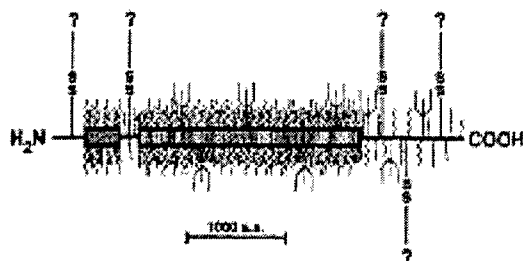


Figure 11. A schematic of mucin (Bansil et al, Ann. Rev. Physiol. Vol. 57, 635-657 (1995)).

As with many other proteins, glycoproteins are also expected to be denatured when exposed to strong acidic or alkaline environments. Near-UV CD spectra of PGM showed that both pH 2 and pH 12 conditions induce a significant change of mucin's tertiary structure, with more pronounced changes at pH 2 than at pH 12. The detailed assignment of peak positions is in progress. These changes in tertiary structure of PGM are directly reflected in their lubrication properties. The COF of PDMS/PDMS sliding is reduced significantly for pH 2 and 12 compared with pH 7. The reduction of friction forces is interpreted to have originated from unfolding of non-glycosylated, "naked" regions of protein backbone and subsequent adsorption onto the hydrophobic surface. The same experiments were repeated by employing a carbohydrate-free protein (human albumin) and a pure carbohydrate (dextran) as aqueous lubricant additives. However, neither of them showed a similar lubricating effect upon changing pH from 7 to 2 or 12 (data not shown). This observation further supports the collective role of hydrophobic (non-glycosylated protein backbone) and hydrophilic (carbohydrate side chains) domains of PGM to function as a boundary lubricant additive at hydrophobic surfaces.

4.2.6 Biotribology: Comparative studies of BSM and PGM

Following the characterization of various interfacial properties of porcine gastric mucin (PGM) at water/PDMS interface, biotribological research was extended to the comparison of different types of mucins. For instance, porcine gastric mucin (PGM) and bovine submaxillary mucin (BSM), which are commercially available, are known to possess some common structural features, i.e. the presence of glycosylated and unglycosylated regions along the linear protein backbone, however, different functions are also expected. Most prominent feature observed in a preliminary study was the opposite pH effect on the aqueous lubrication properties of the gastric (PGM) and oral (BSM) mucins.

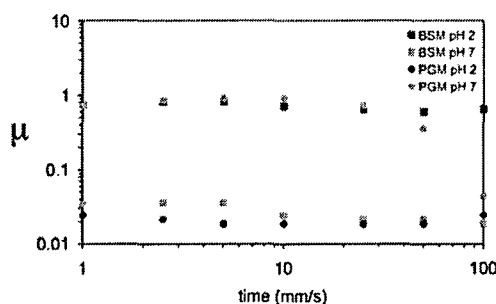


Figure 12. The influence of PGM and BSM on the μ vs. speed plots of PDMS/PDMS sliding contact by means of pin-on-disk tribometry (mucin concentration = 1mg/ml, load = 1N, radius of pin = 3mm).

As shown in Figure 12, PGM functions as an excellent lubricant additive at acidic condition (pH 2), while its lubricating capabilities are negligible at neutral conditions (pH 7). This trend is directly opposite for the case of BSM, which is consistent with our perception of these organs' function.

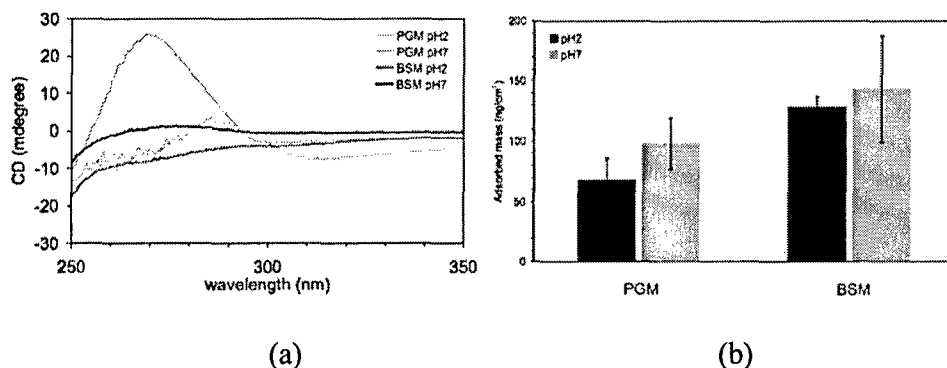


Figure 13. (a) Circular dichroism (CD) spectra and (b) adsorbed mass onto PDMS surface characterized by means of optical waveguide lightmode spectroscopy (OWLS) of PGM and BSM at pH 2 and 7.

While BSM exhibits somewhat higher amount of adsorption than PGM onto PDMS surface both at pH 2 and 7 (Figure 13(b)), the unique pH-dependent lubricating effect of PGM and BSM cannot be explained by their different adsorbed masses. The origin of the difference appears to be more closely associated with the conformation of the two mucins in bulk solution at different pHs; while the unglycosylated region of PGM is strongly folded at pH 7 (strong peak at ~270 nm Figure 2(a)), and start to unfold under pH 2 as judged by near-UV CD spectroscopy, that of BSM is more unfolded at pH 7 than pH 2 (Figure 13(a)). Unfolding of the unglycosylated region of mucins in bulk solution is beneficial not only for stable adsorption, but also for lubrication since it facilitates an ideal conformation of mucin at liquid/solid interface by exposing hydrophilic, brush-like oligosaccharides into bulk water. Further experimental studies are planned to understand the difference of these two mucins in more detail in near future.

4.2.7 Aqueous lubrication of elastomers

The influence of surface modification on the aqueous lubrication of elastomers has been extended by systematically varying hydrophilicity and configuration of the tribopairs involving PDMS. The friction forces arising from elastomeric sliding contacts are generally believed to originate from (a) adhesive components and (b) hysteresis component (imperfect recovery of elastic deformation after sliding contact).

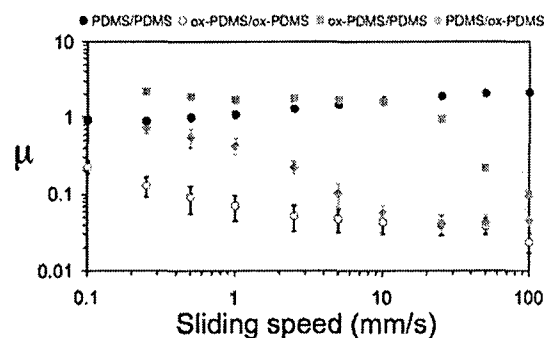
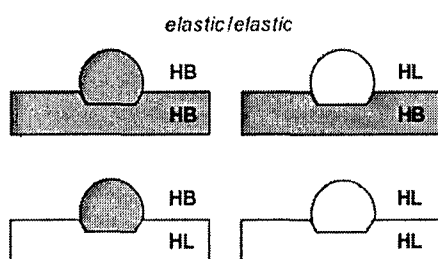


Figure 14. A schematic of four different PDMS/PDMS tribopairs with systematically varying hydrophilicity and μ vs. speed plots obtained in distilled water (load = 1 N).

As shown in Figure 14, systematic variation of hydrophilicity of slider and track revealed that both sides should be rendered hydrophilic (by means of oxygen plasma treatment) to achieve an effective aqueous lubrication. This is due to that the adhesion component mentioned above can be minimized only when both sides are hydrophilic in aqueous environment.

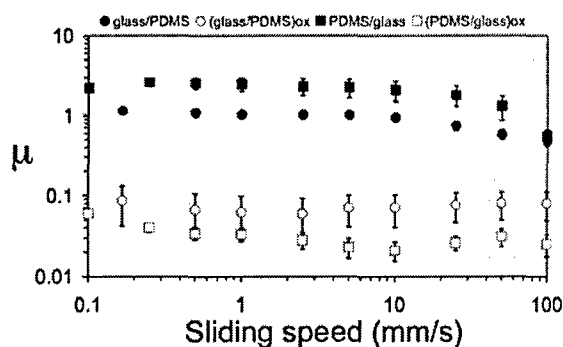
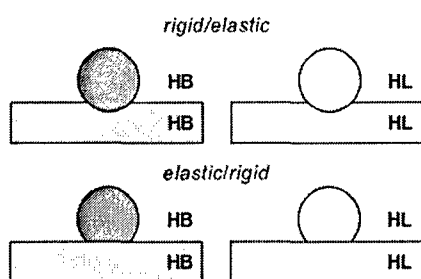


Figure 15. A schematic of four different PDMS-glass tribopairs with systematically varying hydrophilicity and configuration of elastic-rigid contact, and μ vs. speed plots obtained in distilled water (load = 1 N).

Given the hydrophilization of both sides of tribopair a prerequisite for effective aqueous lubrication, another control experiment employing soft-rigid tribopairs (Figure 15) revealed that for asymmetric tribopair composed of elastomer and rigid materials, aqueous lubrication is more effective for a configuration of 'soft slider on rigid track' than 'rigid slider on soft track'. This is due to that hysteresis component for elastomeric sliding friction is absent for the former case.

This study suggests that the design of most effective aqueous lubrication system of elastomers requires a thorough understanding of surface and mechanical properties of the given tribosystem.

4.2.8 Aqueous Lubrication of plastomers

While aqueous lubrication is very effectively achieved at elastomeric contacts through soft-EHL mechanism, rigid plastomers, such as polypropylene (PP), polyamide-6,6 (PA-6,6), and polyethylene (PE), need to be lubricated through boundary lubrication mechanism due to high-pressure asperity contacts. Conventionally, simple surfactants, such as sodium dodecyl

sulfate (SDS), have been considered as a representative aqueous lubricant additive for the polymer/ceramic tribopair. From the previous studies of oxide-based and hydrophobic tribosystems, we note that polyethylene glycol (PEG) immobilized on the surface can act as an effective boundary lubricant as well.

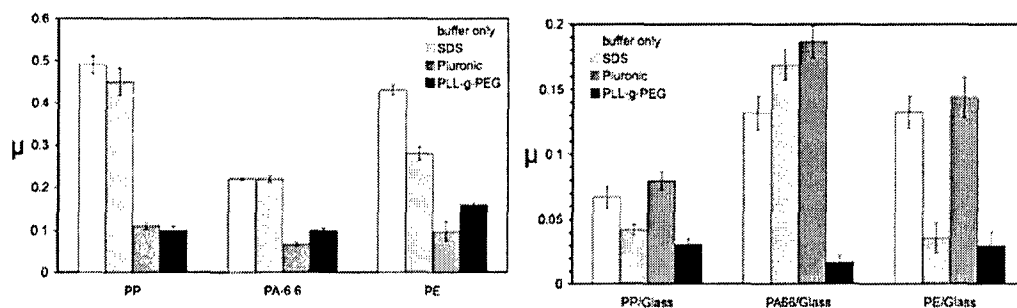


Figure 16. The coefficients of friction of the tribosystems involving plastomers (a) self-mated and (b) polymer/glass pairs (concentration of additives = 0.25 mg/ml, load = 10 N, sliding speed = 5 mm/s, number of rotation = 1,000).

As shown in Figure 16, Pluronic (PEO-PPO-PEO, P105) was most effective at self-mated sliding contacts of various plastomers, probably due to its facile adsorption onto hydrophobic surfaces. Meanwhile, PLL-g-PEG (PLL(350)-g[3.4]-PEG(5)) was most effective at plastomer/glass pairs due to its unique adsorption characteristics to both polar and nonpolar surfaces. These results suggest that surface-bound, brush-like copolymers can be practically used as a boundary lubricant additive at severe contacts involving plastomers as one or both sides of the tribosystems in aqueous environment.

4.2.9 Direct evidence of self-healing effect of PLL-g-PEG at oxide-based tribointerface by means of fluorescence microscopy

In a previous report, we have suggested that the presence of PLL-g-PEG in bulk solution, in addition to a monolayer at the surface of oxide tribosystem, tend to 'self-heal' the tribostressed area due to fast adsorption driven by electrostatic attraction, and thus contribute to remarkable lubricating performance of this polymer. Previously, this assumption was only indirectly argued by comparing the tribological properties the tribosystems with or without PLL-g-PEG in bulk solution. In an effort to verify this idea in a more direct manner, a novel fluorescence-labeled PLL-g-PEG was synthesized. By labeling the polymers at the surface and in the bulk with different kinds of chromophores, we were able to directly visualize the exchange between the polymers at two different places (at surface and in bulk). The results are shown below.

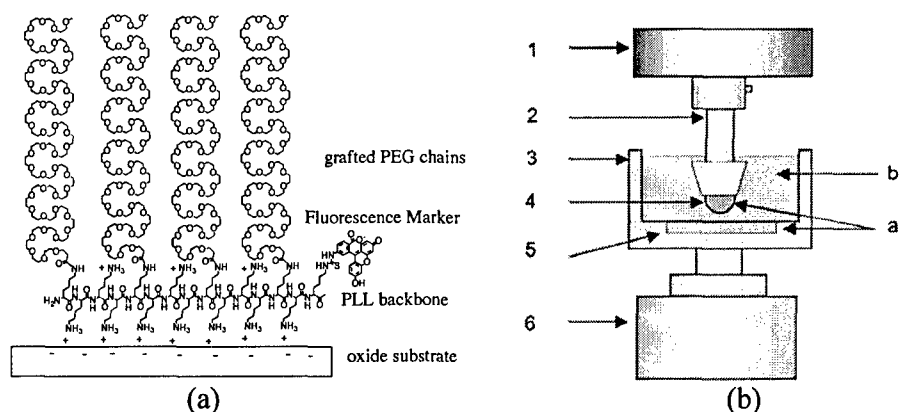


Figure 17. (a) A schematic illustration of PLL-g-PEG/FITC adsorbed onto an oxide substrate surface in an aqueous environment (pH 7). (b) A schematic illustration of the pin-on-disk tribometer (1: dead weight, 2: pin holder, 3: liquid-mode cup, 4: pin, 5: disk, 6: motor) and the location of the two different fluorescence-labeled PLL-g-PEG copolymers (a: fluorescein isothiocyanate (FITC), pre-coating at both pin and disk, b: rhodamine B isothiocyanate (RBITC), in HEPES buffer.

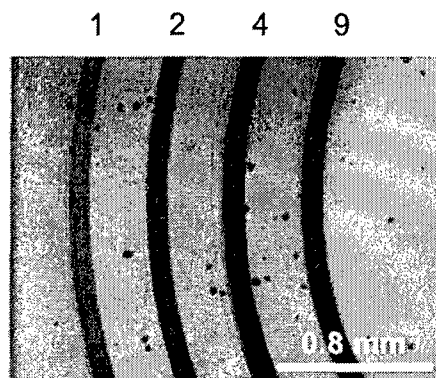


Figure 18. Fluorescence microscopy image of the disk following pin-on-disk tribometry experiment. The number of revolutions was 9, 4, 2, and 1 (in the order of the experiment) in the tracks of radius 1.6, 2.0, 2.4, and 2.8 mm. The load and sliding speed were fixed at 2 N and 5 mm/s, respectively.

4.3. Nanotribology

4.3.1 PLL-g-PEG architecture-dependent behavior of interfacial friction:

Results of these measurements demonstrate the marked dependence of friction on the PEG side chain length, indicating interfacial friction decreases with the increasing PEG side chains. Detailed investigations have revealed the marked PLL-g-PEG architecture dependence of interfacial friction as a function of Lys/PEG grafting ratio of PLL-g-PEG polymers in buffer solution of physiological pH. An investigation on three series of PLL-g-PEG polymers with different PEG side chain length, differing only in Lys/PEG grafting ratio in PLL-g-PEG polymers of each series, revealed that interfacial forces measured for the contact of a

microsphere tip and polymer coated oxide substrates are reduced with decreasing Lys/PEG grafting ratio. The employed polymer series were PLL(20)-g-PEG(1), PLL(20)-g-PEG(2) and PLL(20)-g-PEG(5), with g varying in each series. As a representative result, the friction data obtained from a PLL(20)-g-PEG(2) series are displayed in Figure 19. Combined with the previous results documenting the influence of varying PEG side chain length, the observation of a PLL-g-PEG architecture dependence highlights the opportunity for controlling the tribological properties of interfaces immersed in aqueous solutions through the design and introduction of adsorbed copolymer structures.

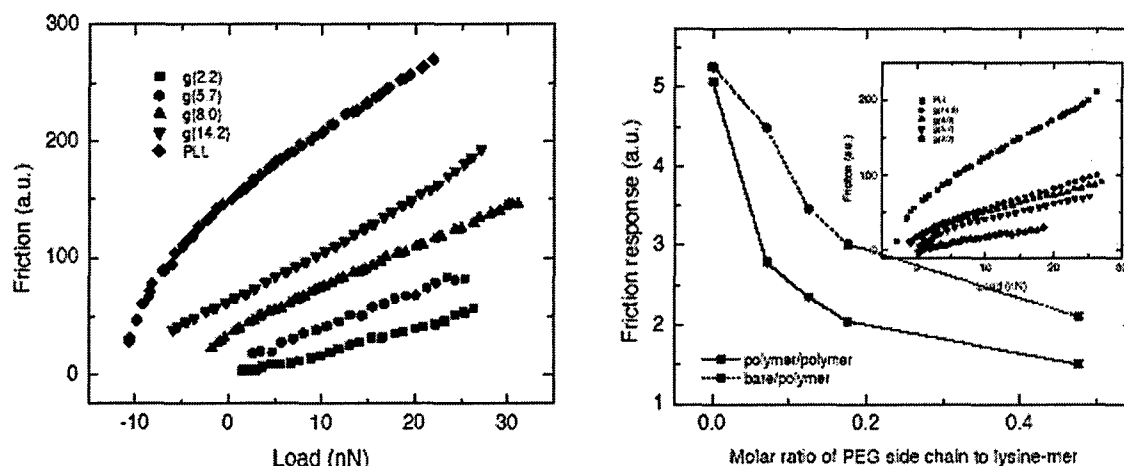


Figure 19. Interfacial friction measured as a function of decreasing load for the contact of a bare microsphere probe and SiO₂ substrates coated with PLL and PLL(20)-g-PEG(2) polymers varying in polymer grafting ratio (lysine-mer/PEG side chains). (a) The corresponding friction response as a function of the molar ratio of PEG side chains to lysine-mer. (b) The data for the contact of the polymer coated SiO₂ surfaces and polymer coated microsphere probe. A single microsphere probe was employed throughout the series of measurements. Lower friction is observed with increasing molar ratio of PEG side chains to lysine-mers.

4.3.2 Substrate dependence of interfacial friction:

Following identical preparation procedures, polymer-bearing surfaces of several kinds of oxides were generated via polymer deposition. As shown in Figure 20, friction measurements on these surfaces showed clear substrate dependence of interfacial friction-- there resulted clear differences in friction among these polymer-coated surfaces even if these surfaces were generated with same polymer under strictly same preparation procedure. AFM images of these oxide surfaces revealed completely flat surface topographies, allowing us to exclude surface roughness as a contributing factor to the measured differences. Taking into account the difference in isoelectric points of the different oxide surfaces, we have correlated lower isoelectric point with lower interfacial friction. Accordingly, we conclude that the difference in polymer surface density results from the difference in the respective IEPs of the different surfaces and gives rise to the difference in friction.

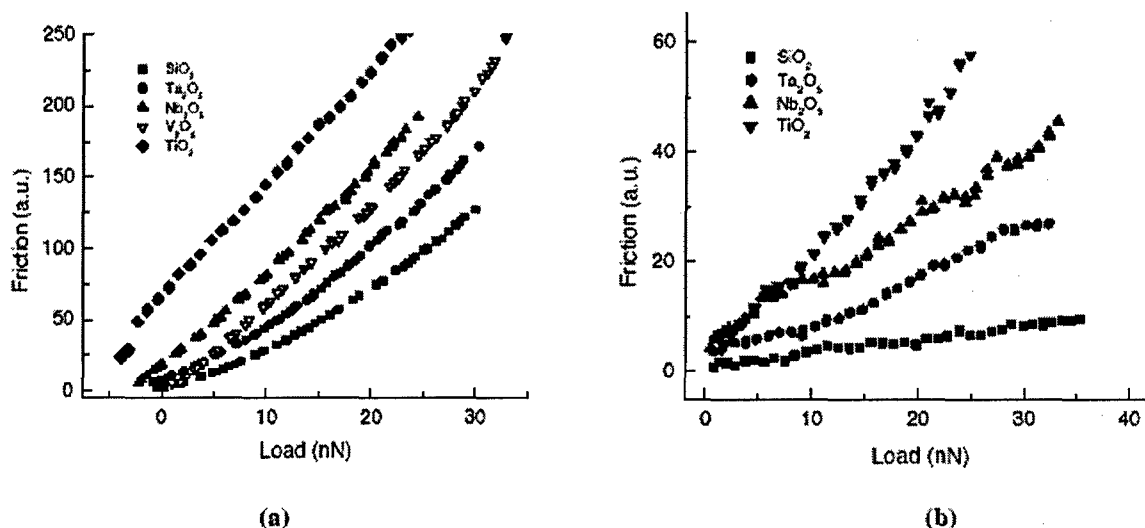


Figure 20. Substrate dependence of interfacial friction measured on PLL(20)-g(3.5)-PEG(5) coated oxide substrates with bare microsphere tip of 10.0 μm in diameter (a) and PLL(20)-g(3.5)-PEG(5) coated microsphere tip of 10.0 μm in diameter (b) in HEPES solution of pH 7.4. These oxide substrates are SiO_2 (2.0), Ta_2O_5 (2.7-3.0), Nb_2O_5 (3.4-3.8), TiO_2 (4.7-6.2), V_2O_5 (?).

Studies have continued at the microscopic and molecular level through the correlated use of atomic force microscopy, QCM, ellipsometry, and optical waveguide light spectroscopy. The combination of these techniques has allowed molecular level insight into the role of solvent in determining/influencing tribological performance of systems involving polymer brushes (biological and synthetic). Significant effort has been expended during the previous year to obtain accurate and quantitative friction data on the microscopic level, thus allowing the determination of specific coefficients of friction for the different systems.

4.3.3 Solvation Effects

The amount of solvent (per unit substrate area) trapped within the tethered, brush-like polymer, referred to as “solvation” (ψ), appears to be of importance in determining the lubrication properties of brush-like polymers. The quantification of the solvency state of brush-like polymers became feasible by a technique combining the individual results of QCM-D and OWLS measurements. In this study we investigated the lubrication properties of the brush-like polymer poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) in function of solvation. For this purpose, solvation was varied by choosing different solvents differing in the solvent quality in respect of the PEG brush (aqueous HEPES buffer solution, methanol, ethanol and 2-propanol) and by changing the volume mixture ratio in the binary solvent mixture of aqueous HEPES buffer solution and 2-propanol.

The mass of surface bound polymers, measured by QCM-D, includes a contribution from solvent molecules that are bound or hydrodynamically coupled to the adsorbed film. This is in contrast to optical techniques, such as OWLS, which are only sensitive to the “dry mass” of a polymer adsorbed onto the surface of the waveguide. Therefore, a greater mass is determined using the QCM-D in liquid than that measured by optical techniques (e.g. OWLS or ellipsometry). By simply subtracting the dry mass derived from OWLS measurements from the “wet mass” derived from QCM-D measurements, it is therefore feasible to determine the mass of

the solvent “trapped” in the brush-like structure of PLL-g-PEG. This quantity, expressed as mass of solvent per unit substrate area, referred to as solvation (ψ), is difficult to measure by other approaches. The raw data of a representative QCM-D and a representative OWLS measurement are shown in Fig.21 and Fig.22, respectively.

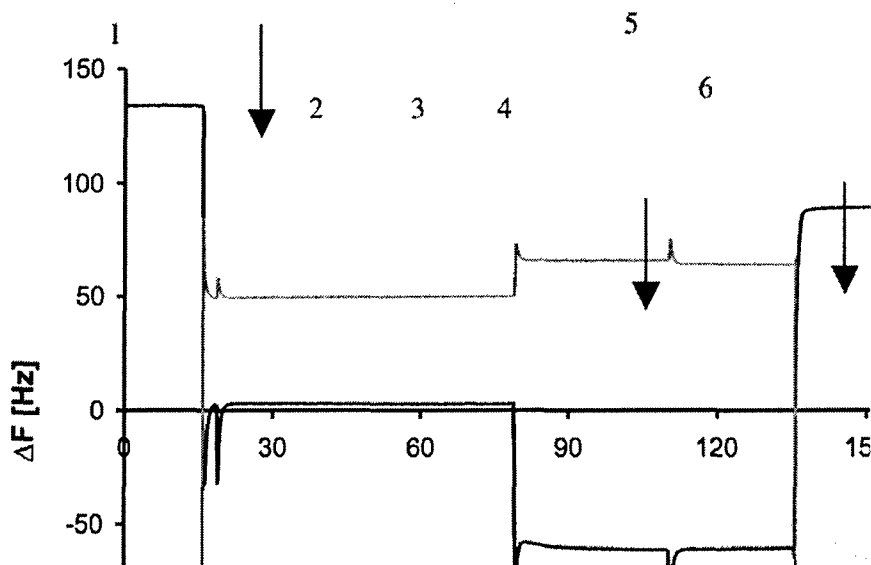


Figure 21.

Changes in the normalized third overtone resonance frequency, ΔF (black line), and dissipation, ΔD (grey line), during adsorption of PLL(20)-g[3.5]-PEG(5) onto a SiO_2 sputter coated surface of the HEPES-methanol system. Before injection of the polymer the baselines of the SiO_2 -coated quartz crystal were measured in methanol and subsequently in HEPES buffer solution. The exchange of methanol for HEPES buffer solution is indicated by the arrow number 1. The injection of the polymer is indicated by the arrow number 2. The measurement chamber was rinsed with polymer-free aqueous HEPES buffer solution 30 mins after polymer injection (arrow number 3). Subsequently, the aqueous HEPES buffer solution was replaced by methanol and the resonance frequency f_0 and the dissipation factor D were measured again (arrow number 4). The reproducibility of the f_0 - and D - shifts upon solvent changes was tested by replacing methanol back by aqueous HEPES buffer solution (arrow number 5) and after 10 min the methanol was replaced back once again by HEPES buffer solution (arrow number 6). The measurement procedure for the HEPES-methanol solvent system described in detail was applied to the other two solvent systems, HEPES-ethanol and HEPES-2-propanol.

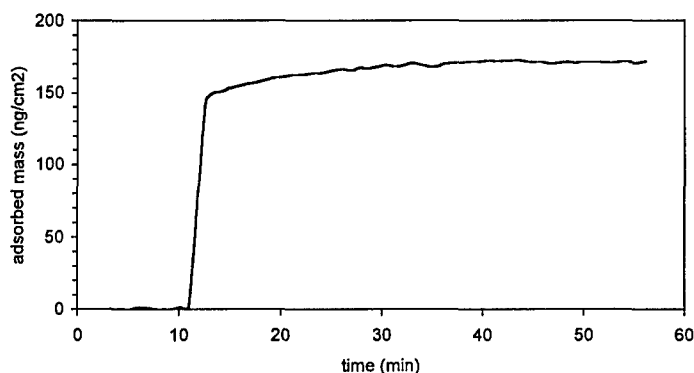


Figure 22. Representative adsorption profile of PLL(20)-g[3.5]-PEG(5) on silicon oxide measured by OWLS.

4.3.4 Solvent Quality Effects

The highest degree of solvation for PLL(20)-g[3.5]-PEG(5) was determined for aqueous HEPES buffer solution, $\psi = 1042.7 \text{ ng/cm}^2$, and a progressive decrease of solvation was observed for methanol $\psi = 678.0 \text{ ng/cm}^2$, ethanol $\psi = 438.8 \text{ ng/cm}^2$, and 2-propanol $\psi = 203.7 \text{ ng/cm}^2$. Solvation of 2-propanol is insignificantly higher than the dry mass of the PLL-g-PEG polymer ($m_{\text{dry}} = 197.84 \text{ ng/cm}^2$) adsorbed onto a silicon oxide surface.

Figure 23 shows friction-versus-load measurements for “symmetric” (both silicon wafer and tip are coated with PLL(20)-g[3.5]-PEG(5)) and “asymmetric” (only the silicon wafer is coated with PLL(20)-g[3.5]-PEG(5)) interfaces under various solvents (aqueous HEPES buffer solution, methanol, ethanol, 2-propanol). In both cases all friction curves show an almost linear dependence on load and run through the origin, indicating that the measurements are not influenced by an adhesion component. Further, a clear dependence of the friction force on the type of solvent is observed over the whole range of load investigated in this study. The friction force is highest for 2-propanol and decreases steeply in the order of 2-propanol, ethanol, methanol and aqueous HEPES buffer solution. Sliding contact of the asymmetric tribosystem showed higher friction forces compared to the symmetric tribosystem, indicating the friction reduction resulted from polymer adsorption at the interfaces of oxides in all liquid media. The results confirm the influence of the nature of solvents on the interfacial friction of PLL-g-PEG modified oxide interfaces.

As depicted in Figure 24, sliding contact of the asymmetric tribosystem, where only the silicon wafer is coated with PLL(20)-g[3.5]-PEG(5), showed throughout higher friction forces compared to the symmetric tribosystem, where both silicon wafer and tip are coated with PLL(20)-g[3.5]-PEG(5). The friction force is highest for 2-propanol and decreases steeply in the order of ethanol, methanol and aqueous HEPES buffer solution. Both tribosystems, asymmetric and symmetric, experience a significant increase in the COF with decreasing solvation. The course of the two curves is highly parallel showing no qualitative differences between the two systems. Thus it is suggested that the molecular friction mechanism of PLL-g-PEG, bathed in solvents of different solvent quality, is not materially different for the asymmetric and symmetric tribopair.

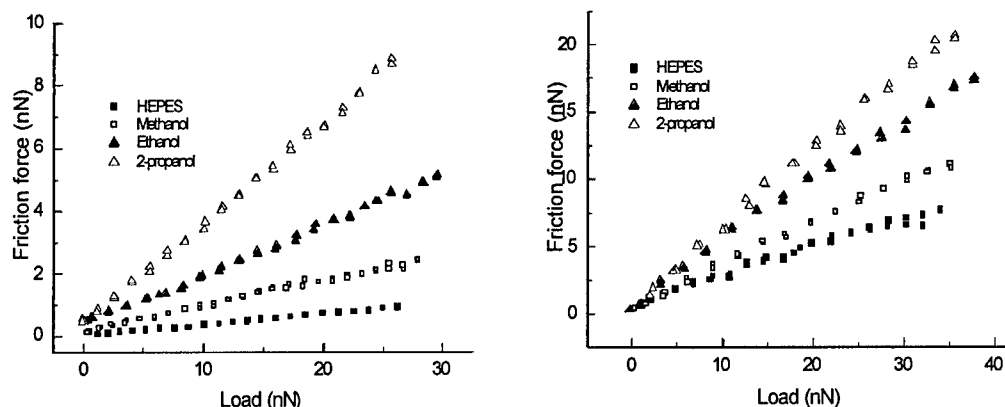


Figure 23. Solvent effect of interfacial friction measured on PLL(20)-g[3.5]-PEG(5) coated SiO₂ interfaces. (a) Friction vs. load plots collected for the interfaces coated with PLL(20)-g[3.5]-PEG(5) on both sides as a function of the nature of solvents and (b) Friction vs. load plots for the interfaces of bare microsphere tip and PLL(20)-g[3.5]-PEG(5) coated SiO₂ substrates as a function of the nature of solvents.

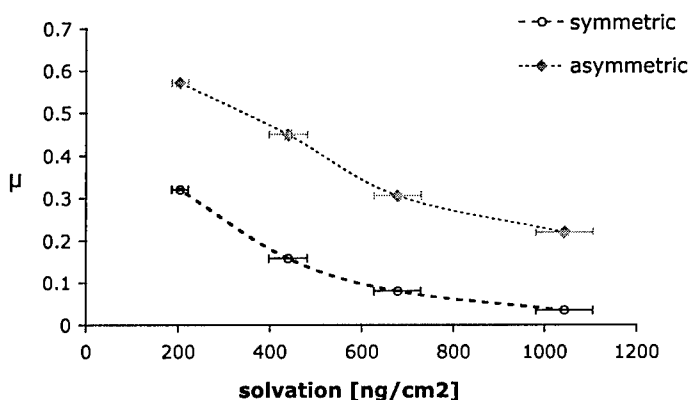


Fig. 24:

The amount of solvent (per unit substrate area) trapped within the tethered, brush-like polymer, referred to as solvation (ψ), vs. coefficient of friction, (μ). Solvation of the PEG brush was varied by choosing four different solvents (aqueous HEPES buffer solution, methanol, ethanol and 2-propanol) differing in the solvent quality in respect of the PEG brush.

4.3.5 Lubrication Properties of PLL-g-PEG in a binary solvent mixture

We investigated on the structural and the frictional properties of PLL(20)-g[3.5]-PEG(5), in contact with solvent mixtures. Mixtures of solvents are more often the rule rather than the exception in engineering applications. Some interesting effects have already been reported theoretically and, to a less extent, experimentally for brushes in binary and ternary mixtures of solvents and these have been rationalized in terms of preferential association of one of the components with the polymer layer. That means that the behavior of a solvent mixture is not simply the combination of the individual properties of the single solvent components but is rather complex. Figure 25 shows the solvation of surface bound PLL-g-PEG in relation to the volume proportion, Φ , of 2-propanol in the binary solvent mixture ($\Phi = 1$, pure 2-propanol; $\Phi = 0$, pure aqueous HEPES buffer solution). One clearly observes that the solvation drastically decreases upon increasing of the 2-propanol proportion above $\Phi = 0.85$, and reaches a value of

$\Psi = 208.7 \text{ ng/cm}^2$ for pure 2-propanol, whereas a variation of Φ in the range of 0 to 0.85 causes a uniform and shallow decrease of the solvation from $\Psi = 1101.3 \text{ ng/cm}^2$ to $\Psi = 761.8 \text{ ng/cm}^2$. The highly solvated and stretched PEG brush thus collapses to a melt-like, poorly solvated, conformation in the very narrow range of 15% of the solvent mixture ratio. Analogous to solvation, the coefficient of friction of an asymmetric tribopair (only the silicon wafer is coated with PLL(20)-g[3.5]-PEG(5)), increases sharply from $\mu = 0.197$ for pure aqueous HEPES buffer solution as solvation exceeds $\Psi = 0.85$ and reaches a value of $\mu = 0.547$ in pure 2-propanol. These observations strongly indicate that the binary mixing ratio of aqueous HEPES buffer solution and 2-propanol is not the same in- and outside the polymer brush, meaning that the polymer brush induces a partial separation of the binary solvent mixture whereas aqueous HEPES buffer solution is preferentially absorbed within the polymer brush. At $\Phi = 0.85$ the discrepancy between the solvent mixing ratio in- and outside the brush cannot be maintained anymore and a further increase of the 2-propanol ratio results in both a progressive collapse of the PEG brush and a considerable increase of the measured friction forces due to a significant decrease of the solvency state of the PEG brush as shown in Figure 26. Thus the superior lubrication properties of PLL-g-PEG prevail in the binary solvent mixture of a good and an inferior solvent quality provided that the volume fraction of the solvent of the inferior solvent quality is kept below a well-defined threshold.

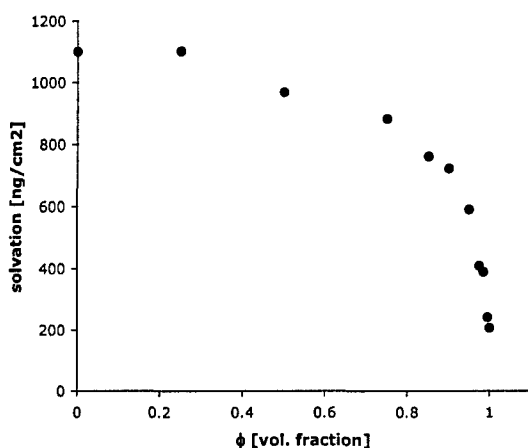


Figure 25. Solvation of surface bound PLL-g-PEG in function of the volume proportion, Φ , of 2-propanol in the binary solvent mixture of aqueous HEPES buffer solution and 2-proanol ($\Phi = 1$, pure 2-proanol; $\Phi = 0$, pure aqueous HEPES buffer solution).

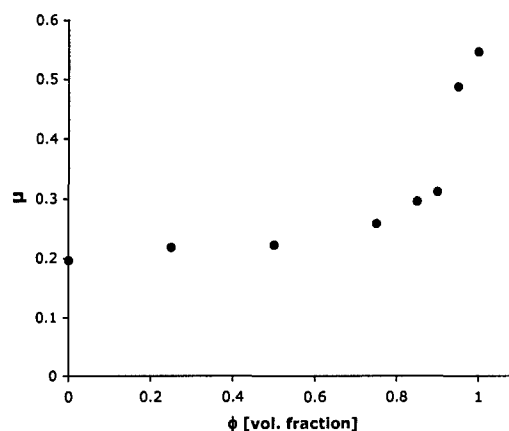


Figure 26. Coefficient of friction, μ , of an asymmetric tribopair (only the silicon wafer is coated with PLL(20)-g[3.5]-PEG(5)) vs. the volume proportion, Φ , of 2-propanol in the binary solvent mixture of aqueous HEPES buffer solution and 2-proanol ($\Phi = 1$, pure 2-proanol; $\Phi = 0$, pure aqueous HEPES buffer solution).

4.3.6 Quantitative Determination of Coefficient of Friction(COF)

The quantitative determination of coefficient of frictions (COF) has been enabled through an experimentally effective force calibration for both normal load and lateral force in AFM measurements. Normal loads have been calibrated directly from the reported spring

constant(0.58N/m) or the calibrated spring constant of AFM cantilevers, while the friction forces have been calibrated through an improved wedge calibration method. Briefly, the lateral force calibration was experimentally made by sliding the AFM tip across a silicon grating surface containing two known slopes (TGG01, MikroMasch, Narva mnt. 13, 10151 Tallinn, Estonia) as a function of applied load.

4.3.7 Frictional properties of PLL-g-PEG with extremely low Lys/PEG grafting ratio.

Following the previous studies concerning the effect of the grafting ratio of PLL-g-PEG polymers with Lys/PEG more than ~ 3.0 , an investigation on PLL(20)-g-PEG(5) polymers with extremely low Lys/PEG grafting ratio($g < 3.0$) has shown an inverse grafting ratio dependent behavior, compared to the grafting ratio effect observed from polymers with relatively high grafting ratio range ($g > 3.0$). As shown in Figure 27, the interfacial friction for the contacts of bare tip and PLL(20)-g-PEG(5) modified substrates increases in the sequence of $g = 3.5, 2.1$ and 1.5 . It is suggested that the reduced number of positive charges of PLL(20)-g[2.1 or 1.5]-PEG(5) available for binding to the surface resulted in lower adhesion strength and less stability of PLL-g-PEG film in buffer solution. As further proof, we also carried out AFM measurements on a SiO₂ surface treated with NH₂-PEG through exactly the same polymer deposition procedure, compared to bare/bare SiO₂ interface, no evident friction reduction was observed for NH₂-PEG treated SiO₂ interface. These results indicate that NH₂-PEG with only one positive charge on the polymer chain end is more weakly absorbed on the oxide surface through electrostatic interactions and thus lessens the likelihood of forming stable brush-like polymer films. It is suggested that there are two factors that play key roles in the lubrication effect of PLL-g-PEG: charge density of PLL backbone and PEG brush areal density. For the polymers with extremely low Lys/PEG grafting ratio, less charge density of PLL backbone plays a dominant role, while for polymers with relatively high Lys/PEG grafting ratio, areal PEG density plays a dominant role.

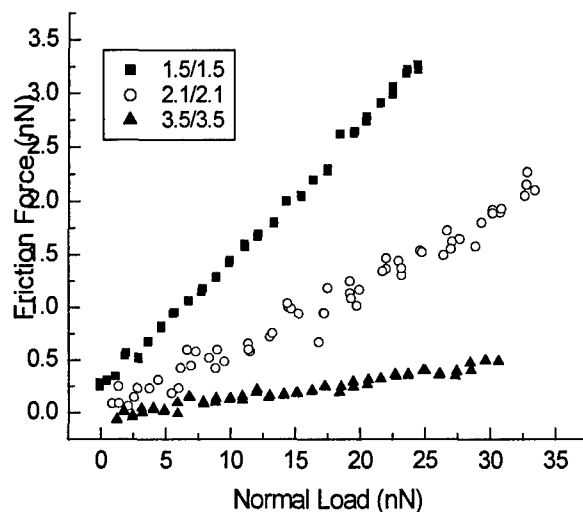


Figure 27. Friction-Load plots for PLL(20)-g-PEG(5) polymers with extremely low Lys/PEG grafting ratio. All the measurements have been performed using same LFM-cantilever assembly modified with a silica microsphere for symmetrically coated tribointerfaces(coated microsphere/coated substrate).

4.3.8 Lubrication Properties of PEG-based polymers: Influence of areal solvation

We investigated the areal solvation and frictional properties of PLL-g-PEG in aqueous solution as a function of polymer structures. As shown in Figure 28, both PLL(20)-g-PEG(5) series and PLL(20)-g-PEG(20) series have shown that increased areal solvation resulted in reduced friction. Similar results were also observed for the contact of bare tips and PLL-g-PEG absorbed silica substrate. It indicated that wetting ability of polymer brushes is closely related to polymer structure- the lower Lys/PEG grafting ratio and longer PEG chain length, the more amount of water trapped in the polymer brushes. However, such a relation of lubrication and areal solvation does not fully rationalize the effects observed for all employed polymers. It is suggested that the areal solvation measurements overestimate the extent of friction reduction for these polymers due to the amount of retained water under compression when tip sliding against the substrate differing from the conditions of the solvation measurements. In addition, the difference in the stability of polymer attachment is another cause to affect the resulting lubrication effect. In conclusion, the amount of retained water under compression is the key factor essentially affecting the lubrication properties of PLL-g-PEG polymer films in aqueous solution.

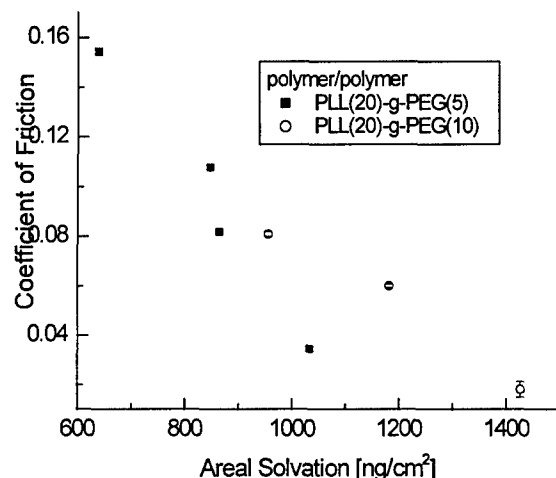


Figure 28. Friction responses as a function of areal solvation, ψ , for polymers differing in both the molecular weight of the PEG side chains and in Lys/PEG grafting ratio, g . In this figure, the Lys/PEG grafting ratio, g , decreases from left to right.

5. Lines of Communication

Communication between scientists at the University of Houston and ETH-Zurich has been facilitated through regular video conferences and email. In addition, Prof. Spencer and Perry have attended a number of meetings together and have taken the opportunity to address programmatic issues at these times.

6. Personnel Supported

University of Houston

Dr. Xiaoping Yan, Postdoctoral Fellow, 100%

Prof. Scott S. Perry, Professor

ETH-Zurich

Prof. Nicholas D. Spencer, Professor

Dr. Seunghwan Lee, Postdoc, 50%

Markus Mueller (Graduate Student) 100%

7. Publications and Presentations

Papers published in refereed journals

Biotribological Approaches to the Lubrication of Engineering Systems

Nicholas D. Spencer, Scott S. Perry, Seunghwan Lee, Markus Müller, Stéphanie Pasche, Susan M. De Paul, Marcus Textor, Xiaoping Yan and Min Soo Lim *Tribological Research and Design for Engineering Systems* (Trib. Ser. 41), 2003

The Influence of Molecular Architecture on the Macroscopic Lubrication Properties of the Brush-like co-Polyelectrolyte Poly(L-Lysine)-G-Poly(Ethylene Glycol) (PLL-g-PEG) Adsorbed on Oxide Surfaces

M. Müller, S. Lee, H.A. Spikes, N.D. Spencer *Tribology Letters*, 2003 (in press)

Boundary Lubrication of Oxide Surfaces by Poly(L-lysine)-g-poly(ethylene glycol) (PLL-g-PEG) in Aqueous Media

Seunghwan Lee, Markus Müller, Monica Ratoi-Salagean, Janos Vörös, Stéphanie Pasche, Susan M. De Paul, Hugh A. Spikes, Marcus Textor, and Nicholas D. Spencer *Tribology Letters*, 2003; 15(3) pp 231-239.

Reduction of friction at oxide interfaces upon polymer adsorption from aqueous solutions

Xiaoping Yan, Min Soo Lim, Scott S. Perry, Nicholas D. Spencer, Stéphanie Pasche, Susan M. De Paul, Marcus Textor, *Langmuir*, 2003, 20(2), 423.

Influence of Molecular Architecture on the Adsorption of Poly(Ethylene Oxide)-Poly(Propylene Oxide)-Poly(Ethylene Oxide) (PEO-PPO-PEO) on PDMS surfaces and Implications for Aqueous Lubrication

S. Lee, R. Iten, M. Müller, and N.D. Spencer, *Macromolecules* 2004, 37(22), 8349-8356.

Preferential solvation and its effect on the lubrication properties of a surface-bound, brush-like polymer

M. Müller, X. Yan, S. Lee, S.S. Perry, and N.D. Spencer, *Macromolecules* 2005, 38, 3861-3866

Lubrication properties of a brush-like copolymer as a function of the amount of solvent absorbed within the brush

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Porcine gastric mucin (PGM) at the water/poly(dimethylsiloxane) (PDMS) interface: Influence of pH and ionic strength on the adsorption and aqueous lubrication properties

S. Lee, M. Müller, K. Rezwan, and N.D. Spencer, *Langmuir* (available as web-released article, July 28, 3005)

Aqueous Lubrication of Polymers: Influence of Surface Modification

S. Lee and N.D. Spencer, submitted to *Tribology International*, 2005 (in press)

Papers submitted to refereed journals

Self-Healing behavior of a polyelectrolyte-based lubricant additive for aqueous lubrication of oxide materials

S. Lee, M. Müller, R. Heeb, S. Zürcher, S. Tosatti, M. Heinrich, F. Amstad, S. Pechmann, and N.D. Spencer, submitted to *Tribology Letters* (July, 2005)

Aqueous Lubrication of Polymers: Influence of Surface Modification

S. Lee and N.D. Spencer, submitted to *Tribology International*, 2004.

8. Interactions/Transitions

Presentations - *Invited*

S.S. Perry

- Division of Polymeric Materials: Science and Engineering, the 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003 **Influence of poly(L-lysine)-g-poly(ethylene glycol) molecular architecture on interfacial shear forces under aqueous environments**
- Division of Colloid and Surface Chemistry, the 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003 **Bio-inspired aqueous lubrication schemes probed on the molecular level**
- Max Planck Institute for Polymers, Mainz, Germany, July 22, 2003, **Bioinspired aqueous lubrication schemes probed on the molecular level**
- DOE Tribology Workshop, March 11, 2004 **Biomimetic lubrication schemes: molecular-level studies**
- Department of Chemical Engineering, University of Texas at Austin, March 24, 2004, **Bioinspired aqueous lubrication schemes probed on the molecular level**

N.D. Spencer

- Leeds-Lyon Symposium on Tribology, Leeds, UK, **Biotribological Approaches to the Lubrication of Engineering Systems**
- AUSTRI, Perth, Australia, **Surface analytical studies of surface-additive interactions, by means of in situ and combinatorial approaches**
- University of Adelaide, Ian Wark Research Center, **Surface Functionalization with Polyelectrolytes for Biosensor and Tribological Applications**
- Department of Physical and Theoretical Chemistry, Oxford University, **Polyelectrolytes on Surfaces: Linkers, Blockers, and Boundary Lubricants**

- ACS National Meeting, New Orleans, **Bioinspired aqueous lubrication schemes probed on the macro level**
- TRIMIS '03, Neuchatel, **Micro- and Nano-scale aspects of Tribochemistry**
- EUROMAT, Lausanne, 1.09.03, **Polyelectrolytes as functional coatings for tribological and bioanalytical applications**
- AVS Annual Meeting, Baltimore Maryland, USA, 2.11.03, **Lubricating with water: biomimetic additives**
- ICMCTF '04, San Diego, 22.4.04, **Lubrication with water: learning lessons from nature**
- IBM Zurich, Seminar, Rüschlikon, Zürich, 16.6.04 **Block copolymers, surface interactions, and aqueous lubrication**
- Sika, AG, Zurich, 13.7.04, **Surface functionalization for tribological and biomaterials applications**

Presentations- Contributed

- Xiaoping Yan, Scott, S. Perry, *225th ACS National Meeting, New Orleans, LA, March 23-27, 2003. Reduction of interfacial friction at oxide interfaces through polymer adsorption* (Poster Presentation)
- Xiaoping Yan, Scott, S. Perry, *2003 Surface Science at round top*, a local conference in Texas **Interfacial friction study on metal oxide surfaces in liquid**
- S. Perry, oral presentation: Tribology Symposium, 227th ACS National Meeting, Anaheim, CA March 29, 2004 **Bio-inspired aqueous lubrication schemes probed on the molecular level**
- S. Lee, poster: "Nanobiotribology: Biological and bio-inspired approaches to lubrication by means of bio-lubricants and controlled surface nano-architecture", *Nanofair 2003*, (St. Gallen, Switzerland, 9-11, September, 2003).
- S. Lee, poster: "Poly(L-lysine)-g-poly(ethyleneglycol) (PLL-g-PEG) as an additive for aqueous lubricant on hydrophobic surfaces", *STLE; Smart Surfaces* (Zürich, Switzerland, 10-12, September, 2003).
- S. Lee, oral presentation: "Boundary lubrication properties of bio- and synthetic polymers containing poly- and oligosaccharides" *American Vacuum Society*, 50th International Symposium and Exhibition (November 2-7, 2003, Baltimore, Maryland, USA)
- M. Mueller, oral presentation: STLE/ASME International Tribology Conference, Florida USA Title: Boundary Lubrication of Oxide Surfaces by Poly(L-lysine)-g-Poly(ethylene glycol) (PLL-g-PEG) in Aqueous Media: Effect of Polymer Architecture, 10/03
- M. Mueller, oral presentation: STLE/ASME Smart Surfaces in Tribology, EMPA Zürich, Switzerland, Title: Investigation of the Physical and Chemical Parameters Determining the Boundary Lubrication Properties of Aqueous Poly(L-lysine)-g-Poly(ethylene glycol) (PLL-g-PEG) Solution, 09/04

- M. Mueller, oral presentation: Q-Sense Scientific Network Meeting, Rönngang Sweden, Title: Influence of the Solvent Condition on the Lubrication Properties of a Brush-like Copolymer, 05/04
- M. Mueller, oral presentation: 1st Joint ETH – UT Seminar, Twente Holland, Title: Biomimetic Lubrication Probed by Lateral Force Microscope, 06/04
- M. Mueller, poster presentation:SVMT Communication between Research, Industry and Society, Title: Bio-inspired Approaches to Aqueous Lubrication by Means of a Surface-Bound, Brush-like Polyelectrolyte, 05/04

Interactions

- Interferometric film thickness measurements in the laboratory of Prof. Hugh Spikes, Imperial College, London

8. New discoveries, inventions, or patent disclosures.

9. New discoveries, inventions, or patent disclosures.

10. Honors/Awards:

Journal of Engineering Tribology, paper of the year award for:

Surface Chemistry in Tribology

A.J. Gellman, N.D. Spencer

Journal of Engineering Tribology; **2002**; 216 pp 443-461

Prof. Scott S. Perry

Promotion to Full Professor

Department of Chemistry and Department of Chemical Engineering

9/1/2003

Prof. Scott S. Perry

Elected vice-chair of Chemistry at Interfaces Gordon Research Conference

8/17/2004

Prof. Nicholas D. Spencer

Elected chair of Chemistry at Interfaces Gordon Research Conference

8/17/2004

Prof. Scott S. Perry

Phi Beta Kappa National Honor Society, Furman University, Alumni Inductee

2005

Prof. Scott S. Perry

Phi Kappa Psi National Honor Society, University of Houston, Faculty Inductee
2005

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